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DEVELOPMENT OF A FLEXIBLE MATERIAL
RESISTANT TO NITROGEN TETROXIDE AND HYDRAZINE

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DEVELOPMENT OF A FLEXIBLE MATERIAL
RESISTANT TO NITROGEN TETROXIDE AND HYDRAZINE

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SCOPE

This report covers the work performed during the period of June 10 to July 9, 1966 on the "Development of a Flexible Material Resistant to Nitrogen and Hydrazine," IITRI Project U6046 under JPL Contract No. 951483.

The primary objectives of this program are to synthesize and evaluate selected fluorinated polymeric systems for utilization as materials of construction for the containment of nitrogen tetroxide and hydrazine-type fuels. The materials and products to be studied and evaluation tests to be carried out are specified in JPL Contract No. 951483.

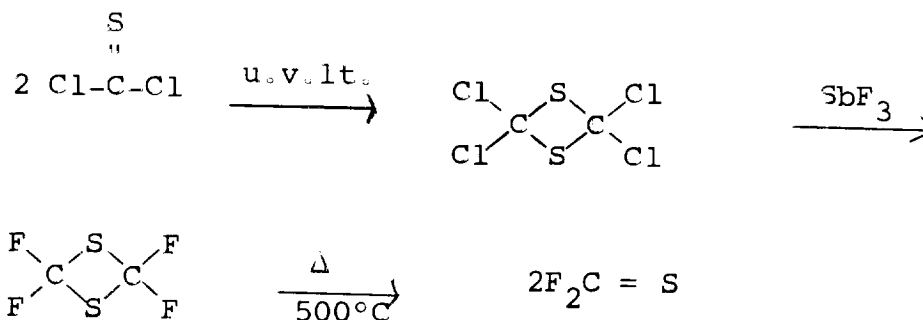
WORK PERFORMED

Preparation of Thiocarbonyl Fluoride

The synthesis of thiocarbonyl fluoride has been undertaken employing the method of Middleton, et al, (ref. 1). This series of reactions (Reaction Scheme 1) involves first the dimerization of thiophosgene by ultraviolet light. To date this dimerization reaction has given very low yields of the tetrachloro-1,3-diethietane, although, we have conducted numerous reactions under varying conditions. In addition, the dimer is rather difficult to isolate in the pure state.

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Reaction Scheme 1

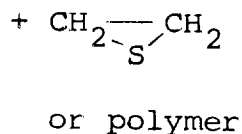
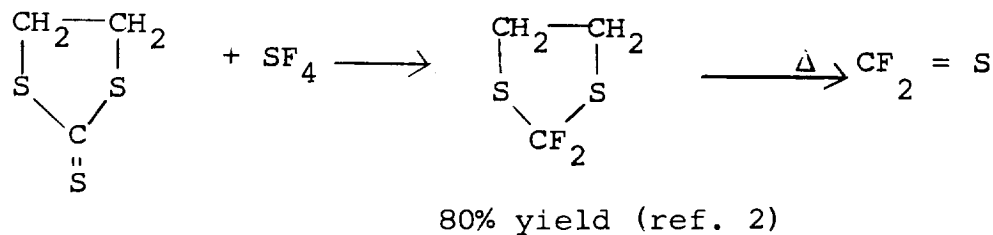


Based on these unsatisfactory results, attention was focused on an alternate method for preparing thiocarbonyl fluoride. Most of the known methods present certain unattractive features for use in the preparation of this compound, particularly from the standpoint of having a readily available supply when needed, since it is considered most difficult to store thiocarbonyl fluoride for extended periods of time in the monomeric state.

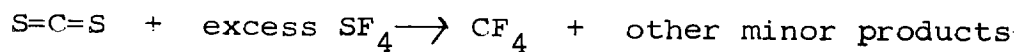
As an alternate means for the preparation of thiocarbonyl fluoride we have been exploring two other methods believed to offer promise as convenient techniques for its synthesis. The first method is concerned with the reductive fluorination of 1,3-dithiolane-2-thione using sulfur tetrafluoride as reported by Smith (ref. 2), followed by pyrolysis at elevated temperatures (Reaction Scheme 2). Approximately seventy grams of the 2,2-difluoro-1,3-dithiolane are available for pyrolysis studies. Providing these latter experiments are successful, this method would allow for the preparation of thiocarbonyl fluoride as

desired from readily available intermediates in a two step reaction sequence.

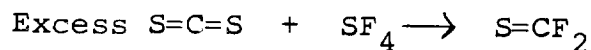
Reaction Scheme 2



The second method selected for investigation is based on the known reaction of sulfur tetrafluoride with carbon disulfide to yield carbon tetrafluoride (ref. 3). Under the appropriate conditions, it would appear possible to control



this reaction to the extent that thiocarbonyl fluoride is the main product since it likely represents an intermediate in the above reaction.



An initial reaction carried out with excess carbon disulfide under static bomb conditions at 110°C have given a product fraction presently being separated and analyzed. Lower temperature transfer of the product fraction indicated the presence of a material boiling in the desired temperature range (\sim -50°C). We also recognize that the most appropriate conditions for a reaction of this type would be a flow system where the reactants would pass quickly through a heated area and the products would be condensed into cold traps. Consideration will be given to such a technique if deemed necessary.

Preparation of Polyanhydrides

Preliminary studies on the synthesis of polyanhydrides from perfluoroglutamic acid were reported last month. These studies have been continued with emphasis being directed towards (a) alternate methods of purifying the commercially available, but impure, acid, and (b) varying the conditions for polymerization of the acid to the polyanhydride.

Perfluorogutamic acid has been purchased from Peninsular Chemical Research, Inc. (Gainesville, Florida) and Pierce Chemical Company (Rockford, Illinois). Both materials were dark colored and obviously impure. Initial efforts to purify the acid involved reprecipitation from alkaline solutions accompanied by a Norit treatment. In addition, we have since employed

sublimation as a technique for purifying the acid with moderate success. The pure acid has been obtained on a small scale after two sublimations. Preliminary attempts to purify the acid via column chromatography through silica gel has been less rewarding due likely to the improper choice of solvent(s) systems. Although further work in this latter area is planned, the sublimation technique will be used for the purification of small quantities of the acid for laboratory scale polymerization experiments.

Polymerization of perfluoroglutaric acid to the polyanhydride has been conducted on a 5.0 gram scale using the technique of Yoda, et al (ref. 4). Several polymerization experiments, including the two reported last month, have been completed under varying conditions, particularly varying reaction times at specified temperatures. A brief description of these reactions is presented in Table 1.

The polyperfluoroglutaric anhydride was obtained as a dark colored solid and/or liquid residue in every instance. This initial discoloration prompted out attempts to obtain a purier grade acid by sublimation, however, the polymer's color did not improve through the use of the sublimed acid. The polymers were all soluble in acetone and dimethylformamide; partially soluble in dioxane and benzene; and essentially insoluble in petroleum ether, hexane and ethyl ether. In most cases, the recovered polymer accounted for approximately

Table 1

Reaction No.	Prepolymerization			Polymerization (Pressure 15-20mm)			
	PFGA (g.)	Ac ₂ O (g.)	Solvent	Reaction Time (Hrs.)	Reaction Conditions Temp. (°C)	Liquid Product (g.) (wt.%)	Solid Product (g.) wt.%
1-5	5.95	44	*Ether	6	Reflux 107-127	1.822	0.50 8.4
1-6	4.40	29.9		7.5	Reflux 139	1.02	0.5 11.5
1-8	6.6	37.3		6.5	R.T.	2.5 All Liquid	All Solid
				**7	180-206		
1-14	5.1	44		7	Reflux 115-135	4.1	80.3
1-15	5.1	44		96	R.T.	**16	
1-16	6.65	44		18	Reflux	3.5	52.6 2.65 39.8
1-17	2.25	44		6	Reflux	0.85	15.8 2.65 49.5
	2.1 Terephthalic Acid Added						

*Acid added to acetic anhydride in an ether solution.

** Pressure >1.0mm.

30-40% of the initial quantity of acid subjected to polymerization indicating that the acid may have been converted partially to the cyclic anhydride or removed by vacuum sublimation at the higher temperatures. The formation of the cyclic anhydride will be investigated on larger scale experiments.

In order to isolate the polymers, the residues were dissolved in a minimum quantity of acetone and petroleum ether added in excess to effect precipitation of a dark colored solid. Evaporation of the filtrate after removal of the solid gave in all cases a viscous liquid residue from which no additional solid could be obtained by reprecipitation. In certain instances, only liquid products were obtained.

The initial prepolymerization reactions (1-5 and 1-6) were conducted at the reflux temperature of the mixture followed by heating at 190-200°C for two hours. The main product was a viscous liquid from which small quantities of solid were isolated. Similar results were obtained in Reaction 1-14. In Reaction 1-16, both the prepolymerization and polymerization times were increased, being 18 and 5 hours, respectively. As a result, the relative quantity of solids increased significantly as well as the total recoverable material.

In Reactions 1-8 and 1-15, the initial prepolymerization reactions were conducted at room temperature. The prepolymerization mixture from 1-8 was heated 2.5 hours at 196-212°C to give an all liquid residue. This residue was subsequently

heated an additional 7 hours at <1mm to yield an all solid product plus a small quantity of solid that sublimed on the walls of the reaction vessel during the heating period. It is interesting to note that this solid product appears to be essentially insoluble in acetone in contrast to the other materials. Other solvents are being sought.

In Reaction 1-15, the polymerization was extended for a period of 16 hours at 1mm during which time a crystalline solid sublimed on the upper walls of the container. Preliminary data indicate the solid to be perfluoroglutaric acid. Again, the residue was mostly insoluble in acetone. Further work in characterizing this product is in progress.

Reaction 1-17 represents an attempt to copolymerize perfluoroglutaric acid and terephthalic acid. The solid product was found to be insoluble in acetone, but dissolves in o-chlorophenol which is being used as the solvent for viscosity data. Further characterization is planned.

Results of the polymerization studies on perfluoroglutaric acid to date indicate that it is possible to obtain a polymer from this dibasic acid. Under the most appropriate conditions the yields likely will exceed 50%, perhaps even higher. The solid products are hard brittle materials having high degrees of coloration and films cast from acetone solutions are extremely brittle. Infrared spectra obtained on films cast from acetone solutions indicate anhydride linkages, however,

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the spectra have been extremely poor in character and band assignments have been difficult to place. As will be discussed in the following section, the polymers are of relatively low molecular weights.

Intrinsic Viscosity Measurements of Polyanhydride

The intrinsic viscosities of polymer samples 1-5 (liquid), 1-5 (solid), 1-6 (liquid), 1-6 (solid) and 1-16 (solid) have been measured in acetone solution at 30°C using a Cannon dilution viscometer, #K369. Viscosity data are presented in Table 2 and plotted in Figure 1.

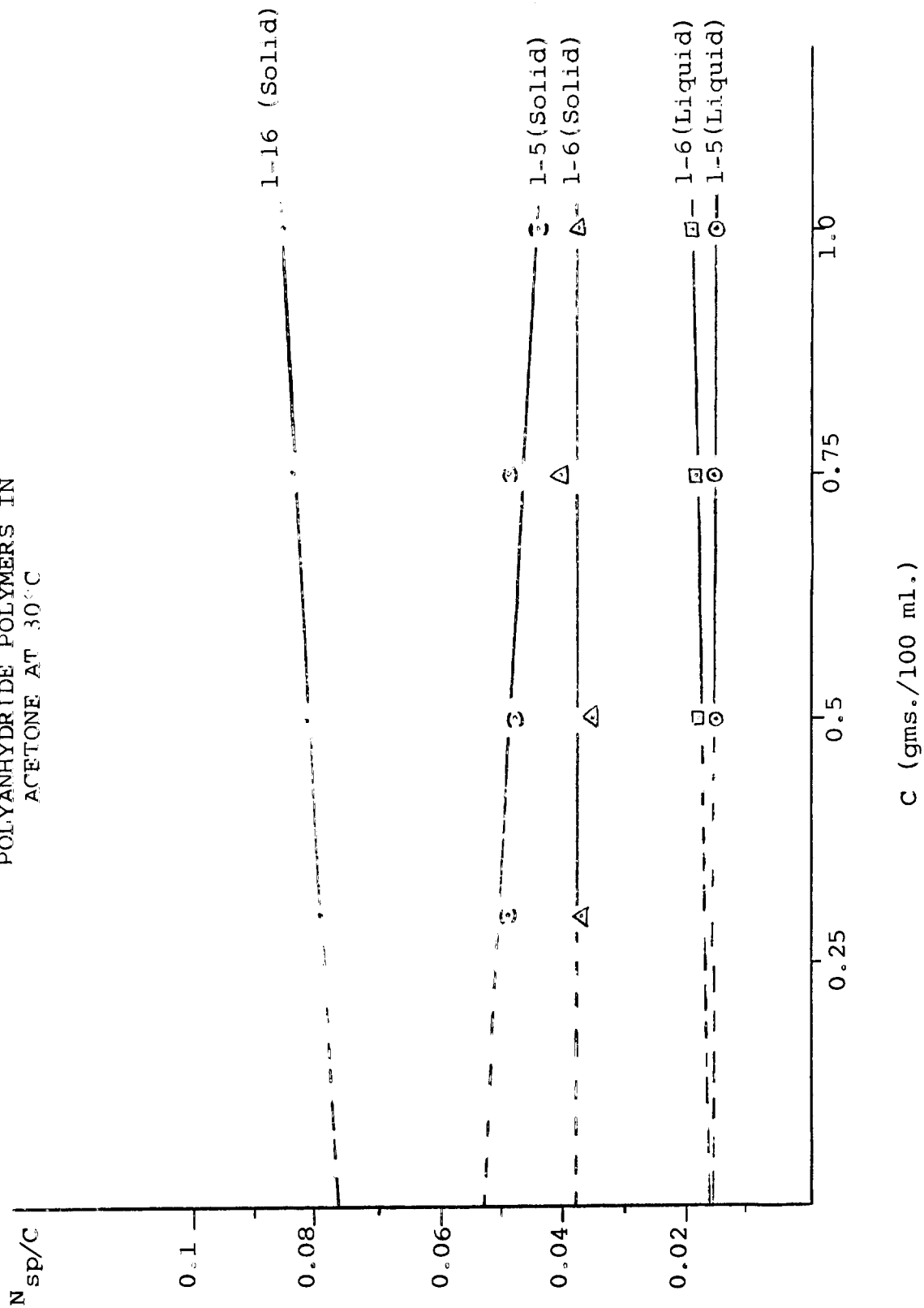
Table 2

<u>Polymer</u>	<u>Intrinsic Viscosity</u>
1-5 (Liquid)	0.016
1-5 (Solid)	0.051
1-6 (Liquid)	0.016
1-6 (Solid)	0.037
1-16 (Solid)	0.079

As shown by the viscosity data, these polymers represent low molecular weight materials. It appears likely that higher molecular weight products are obtainable through increase reaction times or possibly at higher temperatures. In addition, the currently available acetone insoluble polymers may well

Figure 1

PLOT OF N_{sp}/C VS C FOR
POLYANHYDRIDE POLYMERS IN
ACETONE AT 30°C

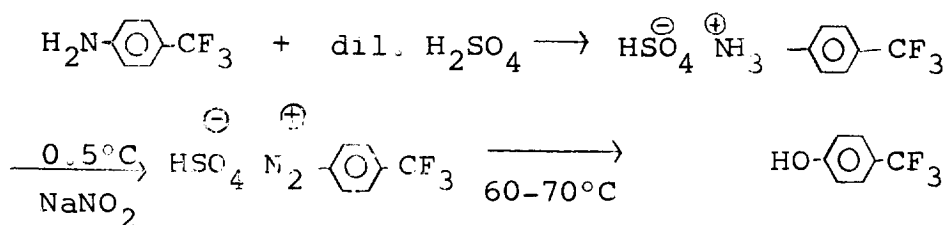


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represent higher molecular weight products and indicates the need to examine the further treatment of these liquid products in attempts to obtain more desirable materials.

Preparation of p-Hydroxybenzotrifluoride

p-Hydroxybenzotrifluoride was thought to be commercially available from either Peninsular Chemical Research, Inc., or Pierce Chemical Company, however, neither source has this chemical at the present time. Synthesis of p-hydroxybenzotrifluoride was carried out by diazotizing p-aminobenzotrifluoride followed by hydrolysis as illustrated by the following reactions.



Purification of the product is presently being completed prior to polymerization studies.

FUTURE WORK

Preparation of Thiocarbonyl Fluoride

The synthesis of thiocarbonyl fluoride by the pyrolysis of 2,2-difluoro-1,3-dithiolane will be examined during the next report period as a means of developing a readily available laboratory source of this compound. Further work on the carbon

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difulfide-sulfur tetrafluoride reaction will depend upon the analytical results of our initial reaction and the success of the above reaction.

Polymers From Thiocarbonyl Fluoride

Depending upon the degree of success in the synthesis of thiocarbonyl fluoride, we plan to study its copolymerization with tetrafluoroethylene at the earliest possible date. These experiments will be initiated as soon as the monomer is available.

Preparation of Polyanhydrides

A larger scale preparative polymerization reaction (15.0 g) of perfluoroglutaric acid is planned in order to obtain sufficient material for compatibility studies with nitrogen tetroxide and hydrazine. The results of the compatibility studies will likely determine to a great extent the future work on polyanhydride systems.

Polymers from p-Hydroxybenzotrifluoride

Polymerization experiments on p-hydroxybenzotrifluoride are planned during the next month. Dow Chemical Company has examined the polymerization of this compound in detail and we plan to use their preferred experimental conditions.

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Polymerization of Octafluorotetrahydrofuran

Both the preparation and attempts to effect polymerization of octafluorotetrahydrofuran are planned during the next few weeks.

Preparation of Perfluorovinyl Perfluoromethyl Ether

The synthesis of perfluorovinyl perfluoromethyl ether will be undertaken as the necessary chemicals arrive. Its preparation involves the addition of trifluoromethyl hypofluorite (available) to 1,2-dichloro-1,2-difluoroethylene (on order) followed by dechlorination.

Respectfully submitted,

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